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THE INFLUENCE OF ABSORBED MOISTURE ON FATIGUE CRACK PROPAGATION--ETC(U)

JAN 81 P E BRETZ, R W HERTZBERG, J A MANSON

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REPORT DOCUMENTATION PAGE

READ INSTRUCTIONS
BEFORE COMPLETING FORM

1. REPORT NUMBER Technical Report #5	2. GOVT ACCESSION NO. AD-A096069	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) The Influence of Absorbed Moisture on Fatigue Crack Propagation Behavior in Polyamides. Part A. Macroscopic Response.		5. TYPE OF REPORT & PERIOD COVERED Interim Technical Report
7. AUTHOR(s) Philip E./Bretz, Richard W. Hertzberg and John A. Manson		8. CONTRACT OR GRANT NUMBER(s) N00014-77-C-0633
9. PERFORMING ORGANIZATION NAME AND ADDRESS Materials Research Center Lehigh University, Bethlehem, PA 18015		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS NR356-670
11. CONTROLLING OFFICE NAME AND ADDRESS Office of Naval Research 800 N. Quincy Street Arlington, VA 22217		12. REPORT DATE January 1981
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office) (12) 35		13. NUMBER OF PAGES 27
		15. SECURITY CLASS. (of this report) Unclassified
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Approved for public release; distribution unlimited

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

Submitted to the Journal of Materials Science

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Polyamides	Fatigue
Effects of water	Fatigue Crack Propagation
	Fracture

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

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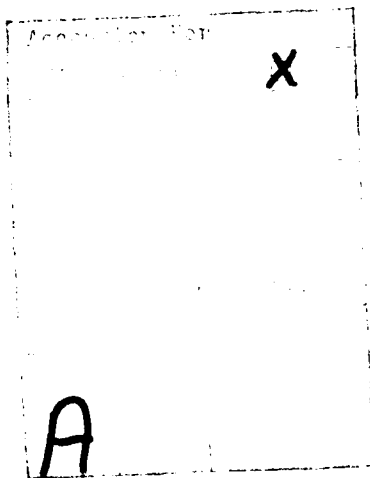
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20. ABSTRACT (continued)

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OFFICE OF NAVAL RESEARCH

Contract N00014-77-C-0633

Task No. NR 356-670

TECHNICAL REPORT NO. 5

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PART A: MACROSCOPIC RESPONSE

by

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Prepared for Publication

in the

Journal of Materials Science

Materials Research Center

Lehigh University

Bethlehem, Pa.

January 30, 1981

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by Philip E. Bretz,¹ Richard W. Hertzberg² and John A. Manson²

Abstract

The effect of plasticization on the fatigue crack propagation response in polyamides was examined by conducting fatigue tests on specimens of nylon 66 (N66), nylon 6 (N6), and nylon 612 (N612) which had been equilibrated at various levels of absorbed water. In N66 and N6, crack growth rates decreased as the water content was increased to about 2.5%; with increasing moisture content, FCP rates increased and at saturation (8.5% H₂O) FCP rates were higher than those observed in the dry polymer. Crack growth rates in N612 decreased monotonically as the water content increased to saturation (3.2% in this polyamide). These results were interpreted in terms of the competition between enhanced crack tip blunting and degradation of the specimen modulus. Crack tip blunting was believed to dominate fatigue behavior at low water contents ($\leq 2.5\%$) and contributed to reduced FCP rates. The higher crack growth rates observed at higher moisture levels were believed to be caused by reductions in material stiffness.

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PART A: MACROSCOPIC RESPONSE

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Introduction

Absorption of water by polyamides represents one important example of the general phenomenon of plasticization of polymeric materials. As such, nylon/H₂O interactions and their associated influence on mechanical response are of considerable engineering importance since absorption of moisture and resulting property changes can occur readily while the nylon component is in service. For example, freshly molded nylon parts contain less than 0.3 wt% water [1], but moisture absorption and consequent plasticization can begin immediately after fabrication if the nylon is not protected from relative humidities (RH) greater than zero. To illustrate this point, roughly 2.5 wt% water can be imbibed after equilibration in a 50% RH ambient atmosphere. Depending on the property and the amount of water absorbed, effects may be beneficial or deleterious.

The incorporation of water in nylon is known to occur in both tightly bound and weakly bound states [2,3]. In the former case, the polar H₂O molecules interrupt the hydrogen bonds between amide groups in neighboring chain segments and create water bridges between these groups. Absorbed moisture is believed to exist primarily in this tightly bound state until all of the hydrogen bonds in the amorphous fraction of the nylon have been replaced by water bridges, corresponding to a water/amide group ratio of 1/2. At higher concentrations, weakly bound water is imbibed and serves essentially as a diluent.

In an earlier publication [4], it was found that fatigue crack growth rates in nylon 66 (N66) exhibited a pronounced minimum at an absorbed moisture content of 2.6 wt% H_2O , while crack growth rates were higher in the saturated material (8.5% H_2O) than in the dry polymer. This minimum was tentatively associated with the transition from tightly bound to loosely bound water at a moisture level between 2 wt% and 3 wt% (for N66 presumed to be 60% crystalline). Subsequently, it was found [5] that the supply of N66 previously considered had a crystalline content of $\sim 40\%$ and that the crack growth rate minimum observed between 2% and 3% water did not correspond precisely to the bound water/free water transition (which occurs at 4-5% H_2O for N66 of 40% crystallinity). In generalizing the results of these two investigations, the decrease in crack growth rates with increasing water content at low moisture levels was interpreted to be associated with enhanced chain mobility and an attendant increase in crack tip blunting. Conversely, the marked increase in crack growth rates at moisture levels $>2.5\%$ was believed to be the result of a degradation of elastic modulus in N66 which accompanies high levels of loosely bound absorbed water [1,6].

In the present study, the generality of the effect of absorbed moisture on the fatigue crack propagation response in nylon was examined by conducting an extensive series of fatigue experiments on other polyamides [a higher molecular weight N66, nylon 6 (N6), and nylon 612 (N612)] which were prepared with a wide range of imbibed moisture. In addition, modulus data as a function of absorbed moisture were obtained from an automated Rheovibron instrument for each of these polyamides; FCP rates were then examined in terms of these dynamic property measurements.

Experimental Procedure

Materials

The nylon fatigue specimens were equilibrated at several moisture levels by soaking plaques in various aqueous salt solutions or by vacuum drying.

Tables 1-3 list the equilibration procedures for each nylon supply. Moisture contents (relative to a dry specimen) were measured gravimetrically for all specimens. For the nylon supplies received with unknown moisture levels, plaques were vacuum dried for varying time periods until no further weight change occurred; the weight lost by these samples was then taken to represent the original moisture content in the as-received condition. After moisture equilibration, all specimens were stored at the appropriate humidities prior to fatigue testing.

The molecular weights (MW) of the N66 and N6 supplies before and after the equilibration procedures were determined by solution viscometry using a Cannon-Ubbelohde dilution viscometer; molecular weights were calculated from measured intrinsic viscosities using the Mark-Houwink equation:

$$M_n = K^{-1/a} [\eta]^{1/a}$$

where M_n = number average MW
 $[\eta]$ = intrinsic viscosity

The constants for this relationship at 25°C were:

for N66[8] $K = 1.1 \times 10^{-3}$; $a = 0.72$ (in formic acid)

for N6[9] $K = 22.6 \times 10^{-3}$, $a = 0.82$ (85% formic acid in water)

Dynamic moduli were determined on an Autovibron apparatus (Model DDV-III-C, IMASS Corporation, Hingham, Massachusetts) at 11 Hz. Test specimens were nominally 2 mm thick x 5 cm long, with the width equalling the thickness of the plaques from which these bars were cut. All tests were performed in laboratory air at a heating rate of 1°C/min., the initial temperature being -20°C to 0°C.

Fatigue Test Procedures

Fatigue test specimens were of either the compact tension (CT) or wedge opening load (WOL) configuration [10]. A mechanical notch was introduced with a jeweler's saw and followed by sharpening with a razor blade to accelerate crack initiation. The fatigue tests were performed on an

%RH	wt% H ₂ O	Method
0	<0.2	As-molded ("dry")
35	1.5	Boiled for 120 hr. in saturated aqueous sodium acetate [7]
50	2.6	Boiled for 100 hr. in aqueous potassium acetate [1]
100	8.5	Boiled for 190 hr. in water [1]

Table 1 - Moisture Conditioning Procedure
for N66 ($M_n = 34,000$)

%RH	wt% H ₂ O	Method
0	<0.2	Vacuum dried for 168 hr. at 95°C
45	1.1	As-received
100	3.2	Boiled for 100 hr. in water [1]

Table 2. - Moisture Conditioning Procedure
for N612

%RH	wt% H ₂ O	Method
0	<0.2	Vacuum dried for 168 hr. at 95°C
50	2.5	As-received
52	2.7	Boiled for 120 hr. in saturated aqueous sodium acetate [7]
100	8.7	Boiled for 190 hr. in water [1]

Table 3 - Moisture Conditioning Procedure
for No

electrohydraulic closed loop testing machine using a 10 Hz sinusoidal waveform of constant load amplitude and a minimum-to-maximum load ratio (R) of 0.1. Duplicate tests were conducted for most material and test conditions, with all tests being performed in laboratory air at $\sim 22^{\circ}\text{C}$ and in an average ambient relative humidity of 40% (except as noted in the text below).

Before any fatigue data were obtained, each specimen was precracked to create a sharp fatigue crack beyond the mechanical notch. The precracking procedure varied for different polymers, but generally was conducted at 50 or 100 Hz. On occasion, precracking loads were set higher than the load range used during actual testing so as to accelerate initiation of the fatigue crack. However, no crack growth data were obtained until the fatigue crack had grown several millimeters past the precracked zone at the subsequent test load range [11]. When crack tip heating occurred as a result of the high frequency precracking procedure, data collection was delayed for at least 30 min. to allow the crack tip region to cool to ambient temperature.

Crack growth was measured optically using a Gaertner traveling microscope with 50X capability. The FCP test was interrupted periodically for 5-10 sec. to record the crack tip position and associated number of cycles; these interruptions occurred typically after crack growth increments of 0.25-0.50 mm.

Incremental crack growth rates were calculated as follows:

$$\left(\frac{da}{dN}\right)_i = \frac{a_{i+1} - a_{i-1}}{N_{i+1} - N_{i-1}}$$

where a = crack length and N = number of cycles. Crack growth rate data were compared with the crack tip stress intensity factor range, ΔK , which is given by

$$\Delta K = Y \frac{\Delta P}{BW} \sqrt{a} \quad [\text{MPa} \sqrt{\text{m}}] \quad (\text{CT})$$

or

$$\Delta K = Y \frac{\Delta P}{B\sqrt{W}} (\alpha) \quad [\text{MPa} \sqrt{\text{m}}] \quad (\text{WOL})$$

where P = applied load range (Newtons); B = thickness (meters); W = width (meters) and Y and α are the geometric correction factors given below.

$$Y_{\text{CT}} = 29.6 - 185.5(a/W) + 655.7(a/W)^2 - 1017.0(a/W)^3 + 638.9(a/W)^4$$

$$Y_{\text{WOL}} = 0.8072 + 8.858(a/W) - 30.23(a/W)^2 + 41.088(a/W)^3 - 24.15(a/W)^4 + 4.951(a/W)^5$$

$$\alpha_{\text{WOL}} = \frac{2 + (a/W)}{[1 - (a/W)^{3/2}]}$$

Test results revealed that da/dN depended on ΔK with a relationship of the form [12]

$$da/dN = A (\Delta K)^m$$

Experimental Results

The effect of absorbed water on FCP rates in N66 (MW=34,000) is shown in Figure 1, based mainly on single-specimen results from each test condition. As was the case with a lower-MW N66 (MW=17,000) [4,5], crack growth rates were lowest for a specimen containing an intermediate level of moisture (1.7 wt% H₂O), and were highest in the saturated material (8.5% H₂O). Figure 2 shows a plot of crack growth rate values at a constant ΔK of 3 MPa \sqrt{m} as a function of moisture level; the solid lines represent data from reference 5 for N66 with MW=17,000 and the data points correspond to the present results for MW=34,000. It is clear from this figure that both supplies of N66 exhibited a minimum in crack growth rate at an intermediate moisture level. Interestingly, while the nylon 66 samples with MW=34,000 exhibited lower FCP rates than N66 (MW=17,000) in the dry condition (Figure 2 and ref. 13), there was no difference in crack growth rates between these materials when saturated with water.

The influence of moisture content on the FCP behavior of N6 parallels that of N66. These results are shown in Figure 3, while a comparison of growth rates at a constant ΔK of 2.5 MPa \sqrt{m} is given in Figure 4. Again, a minimum in FCP rates is apparent at approximately 2.5% water. On the other hand, no FCP minimum as a function of moisture content is found in N6 at higher ΔK levels above about 3 MPa \sqrt{m} . Also note that the crack growth rate for N6 containing 2.7% water is more than 10X larger than for a specimen which absorbed 2.5% water despite the relatively small difference in moisture content.

The FCP behavior of N612 differs from the behavior of the other nylons in that a small but continuous decrease in crack growth rates occurs as the moisture level increases to saturation (Figures 5 and 6). It may be significant, however, that the saturation level in N612 (3.2% H₂O) is close to the moisture level corresponding to the minimum FCP rate in both N66 and N6.

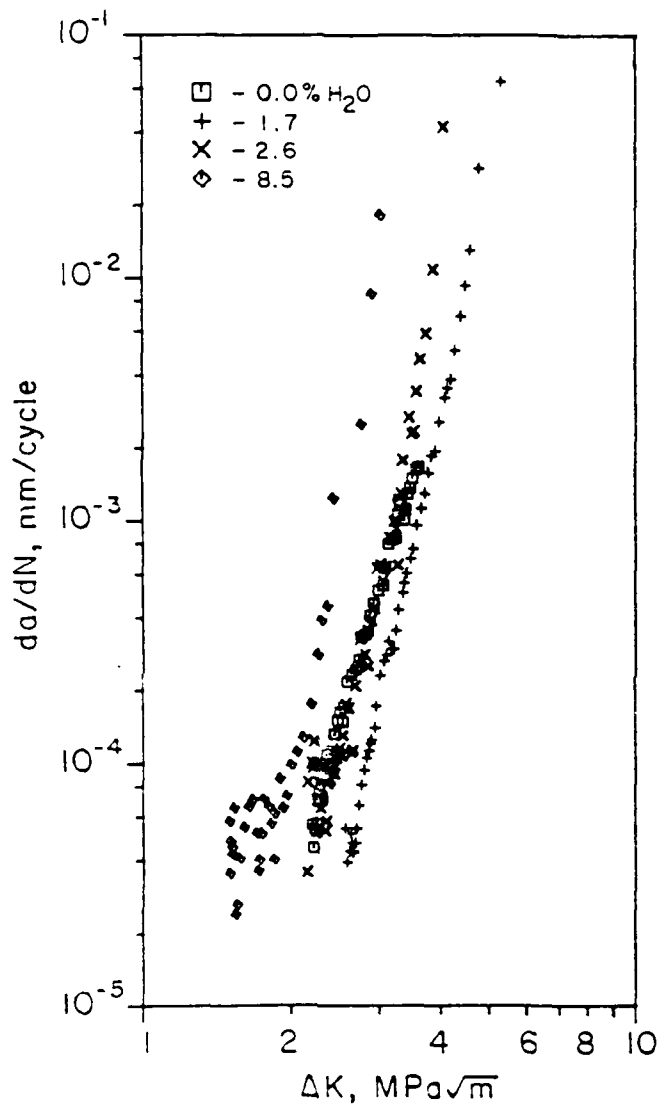


Figure 1 - Effect of moisture on fatigue crack growth rates in N66 ($M_n = 34,000$).

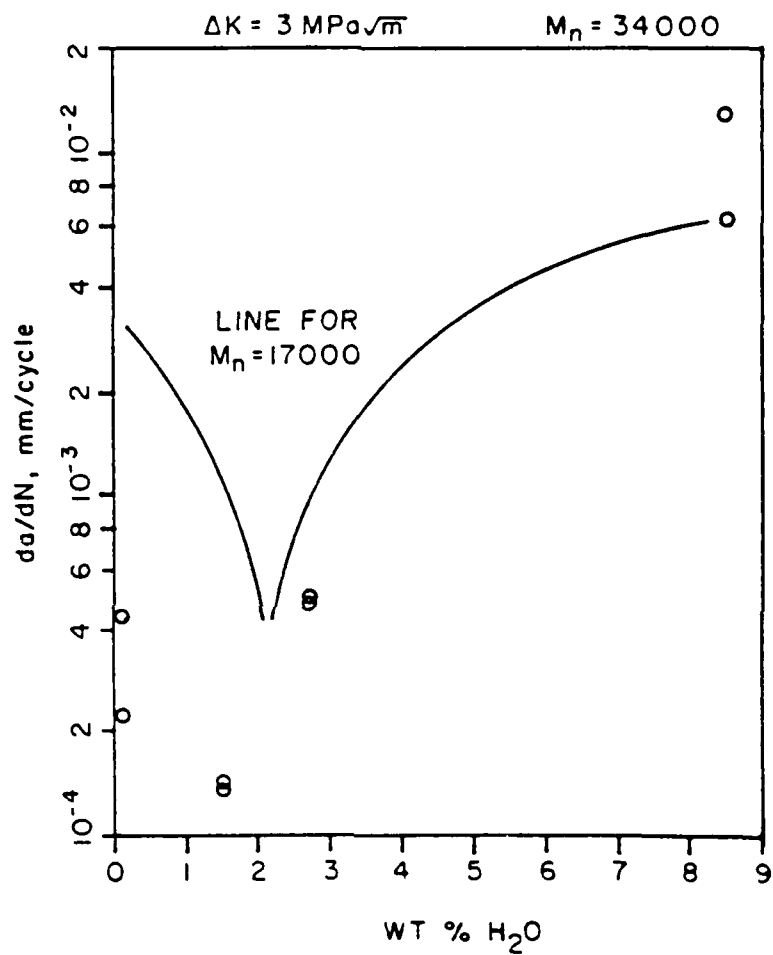


Figure 2 - Fatigue crack growth rates at constant ΔK as a function of moisture in N66 ($M_n = 34,000$).

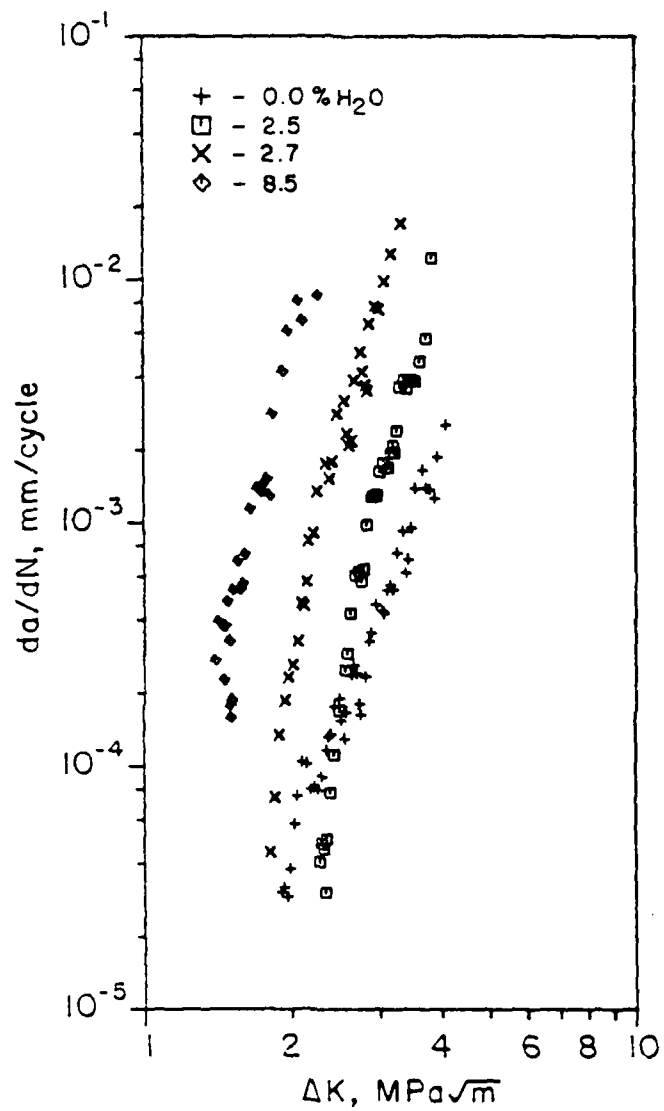


Figure 3 - Effect of moisture on fatigue crack growth rates in N6.

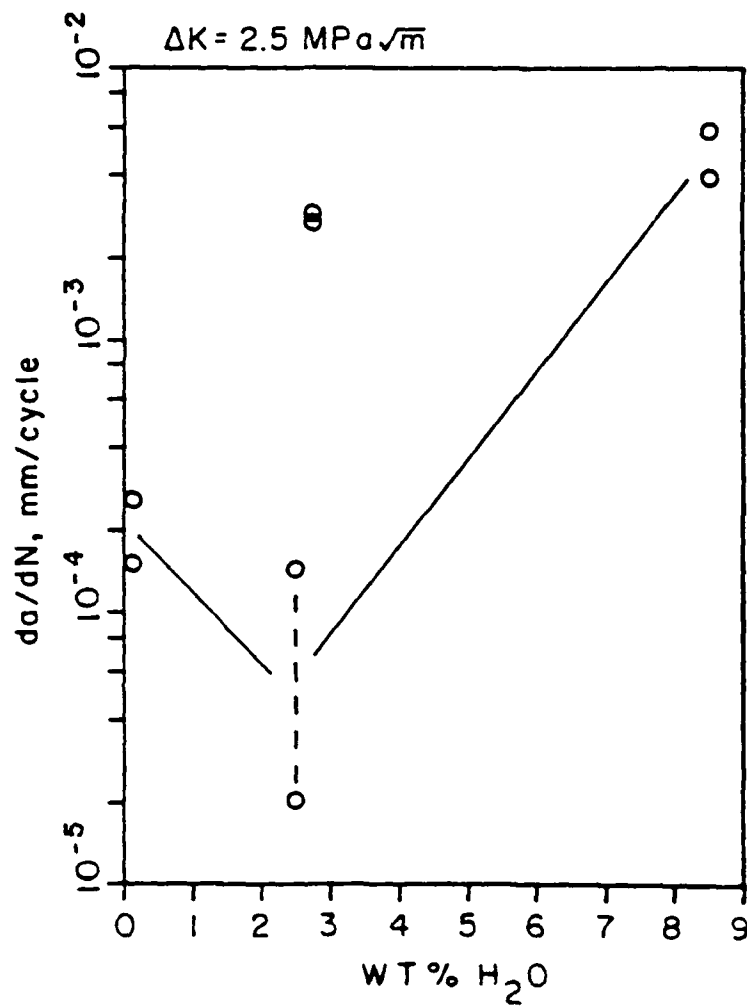


Figure 4 - Fatigue crack growth rates at constant ΔK as a function of moisture in N6.

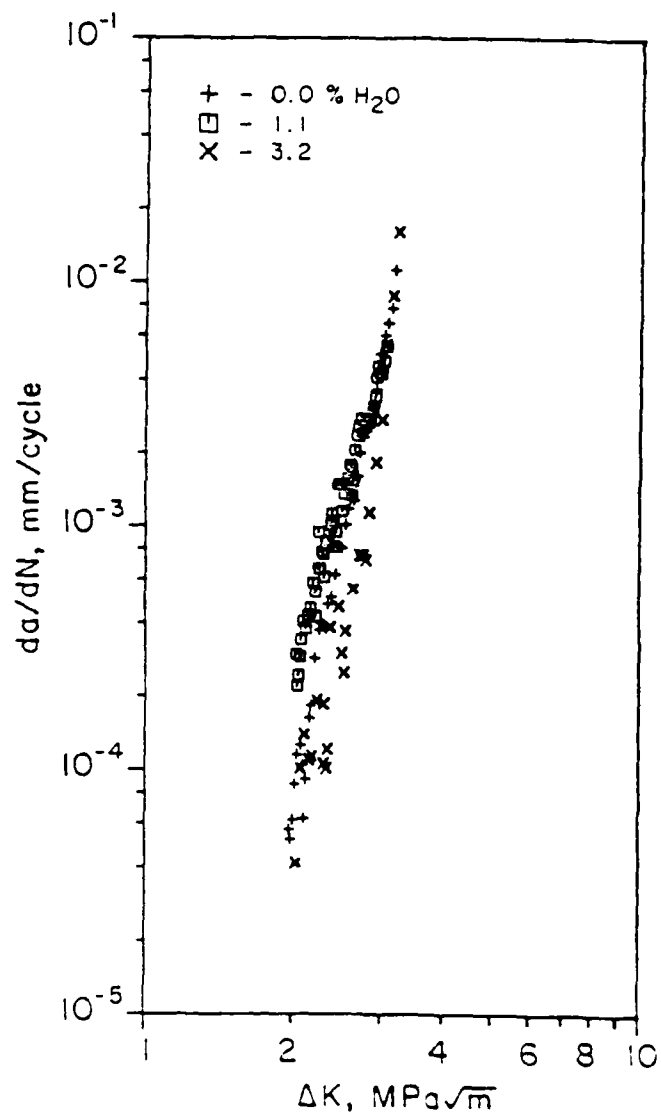


Figure 5 - Effect of moisture on fatigue crack growth rates in N612.

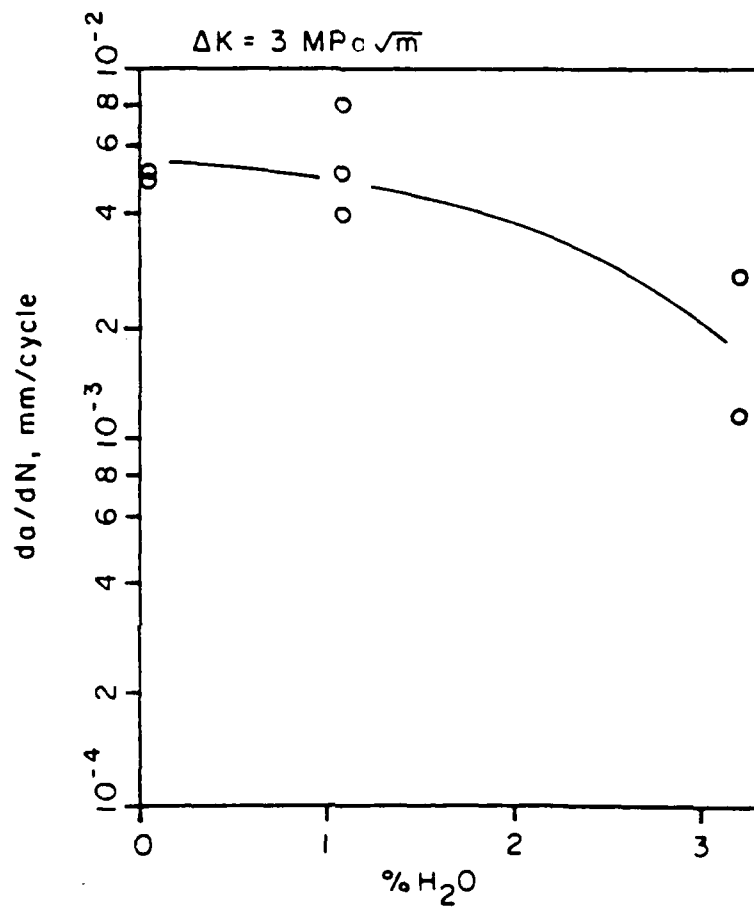


Figure 6 - Fatigue crack growth rates at constant ΔK as a function of moisture in N612.

It was observed previously [5] that the crack growth rate minimum in N66 (at an intermediate moisture level) corresponded to a maximum in relative toughness as measured by the maximum stress intensity level

$(K_{cf} = \frac{\Delta K_{max}}{1 - R})$ attained prior to unstable fast fracture. Though K_{cf} values are not considered to be accurate measures of fracture toughness, they do provide a basis for a relative comparison of material properties. When specimens fail in fatigue by slow tearing rather than by abrupt separation, no such estimate of fracture toughness is possible; such was the case for water saturated N66 (MW=34,000) and for all N6 specimens except the dry test plaques. Table 4 shows that the toughness of N66 with both molecular weights is definitely greater in specimens containing intermediate water levels, corresponding to the lowest FCP rates recorded in these polymers. This finding is consistent with the generally observed tendency for FCP rates to be lower in those polymers that exhibit greater fracture toughness [14,15]. In N612, no variation in toughness was found with increasing moisture content, which parallels the minimal change in FCP rates measured over this moisture level range.

Discussion of Results

In an earlier publication [5], it was tentatively concluded that the effect of absorbed moisture on crack growth rates in N66 (MW=17,000) reflected a competition between crack blunting and a decrement in the room temperature modulus of N66. Certainly even small amounts of absorbed moisture must increase segmental mobility and enhance crack blunting, thus reducing the effective stress concentration and lowering the rate of crack propagation. Such an effect was reported by Bragaw [16] in studies of environmental stress cracking in medium-density polyethylene. However, with increased moisture levels, the room temperature modulus is expected to decrease [1,5,6] thereby increasing the

N66				N612	
$M_n = 17,000$		$M_n = 34,000$			
$\%H_2O$	K_{cf}	$\%H_2O$	K_{cf}	$\%H_2O$	K_{cf}
0	3.2	0	4.2	0	3.6
0.8	3.1	1.7	6.6	1.1	3.6
2.2	7.2	2.6	4.9	3.2	3.6
2.6	5.2				
4.0	4.3				

*Reference 5

Table 4 - Apparent Toughness (K_{cf}) vs. Moisture Level
for N66 and N612.

cyclic strain range under cyclic-load-controlled test conditions; increased crack growth rates should result from the latter circumstance.

Dynamic mechanical spectra for N66 (MW=17,000 and 34,000) and N6 are shown in Figures 7 and 8 and reveal the expected decrease in room temperature modulus with increasing moisture content. It is interesting to note that, for both N66 and N6, the room temperature modulus did not decrease appreciably until after ~ 2.5 wt% water was absorbed. Coincidentally, crack growth rates also began to rise after this moisture level was exceeded. Apparently, the growth rate minima represent an optimization of the competitive influences of crack blunting and modulus degradation. Also, it is significant that the room temperature modulus of N6 containing 2.7% H₂O was nearly three times lower than for a specimen equilibrated at 2.5% (Figure 8), and that crack growth rates in the 2.7% H₂O material were much higher than in the 2.5% plaque (Figure 4). The reason for this large drop in modulus over a very small moisture range is not known at this time, but the correlation between decreased specimen modulus and higher FCP rates is both striking and consistent with expectations.

Previously it was postulated that crack tip blunting should decrease crack growth rates. To examine more directly the specific effect of imbibed moisture-induced crack tip blunting on crack growth rates, FCP data were normalized with respect to modulus (i.e., by plotting da/dN vs. $\Delta K/E$). Figure 9 clearly shows that the value of $\Delta K/E$ necessary to drive the fatigue crack at a given velocity increases monotonically with increasing moisture level; that is, moisture-induced crack tip blunting serves to decrease the material's FCP rate for a given driving force condition.

In summary, the complex effect of absorbed water on FCP rates in N66 and N6 reflects a competition between the beneficial influence of

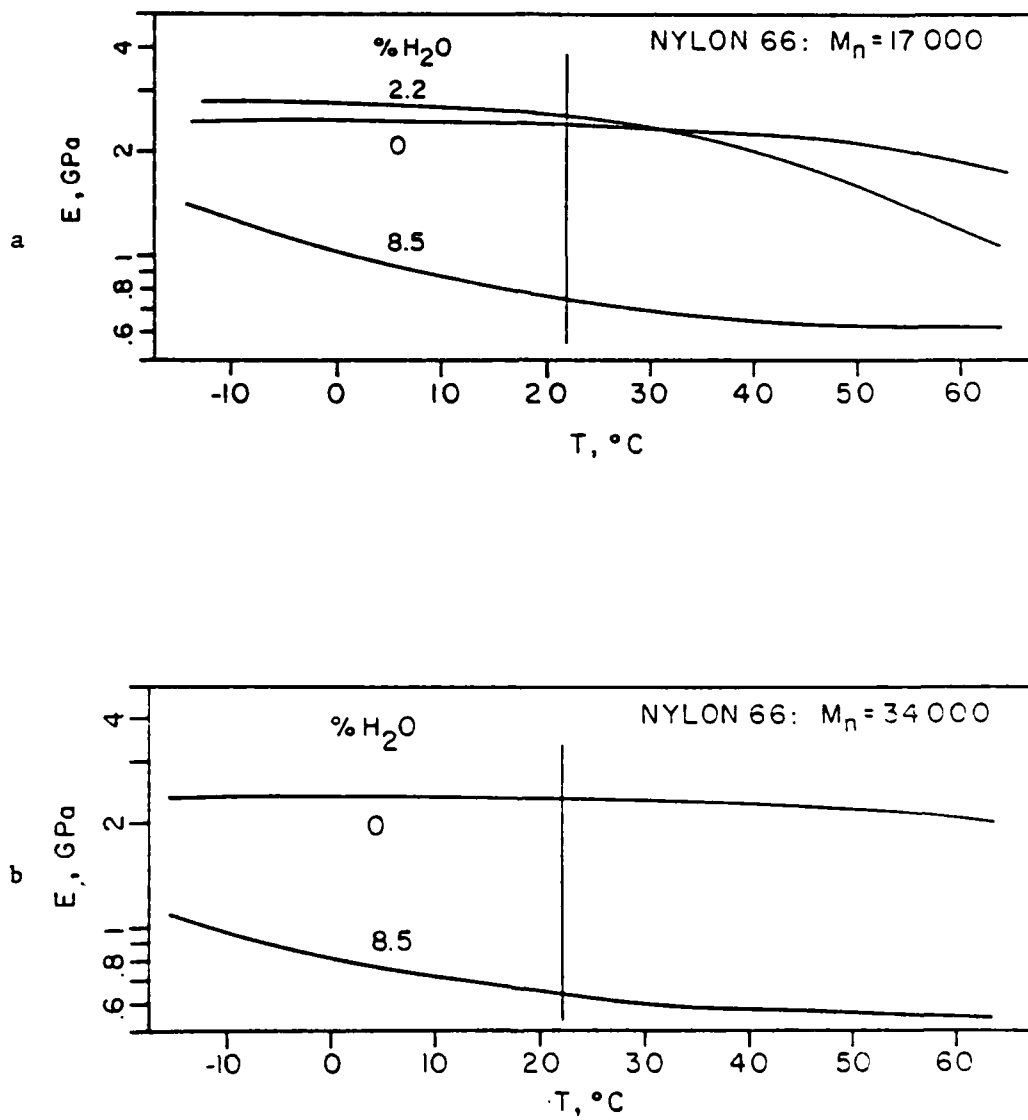


Figure 7 - Modulus as a function of temperature for various moisture levels in N66. a) $M_n = 17,000$; b) $M_n = 34,000$.

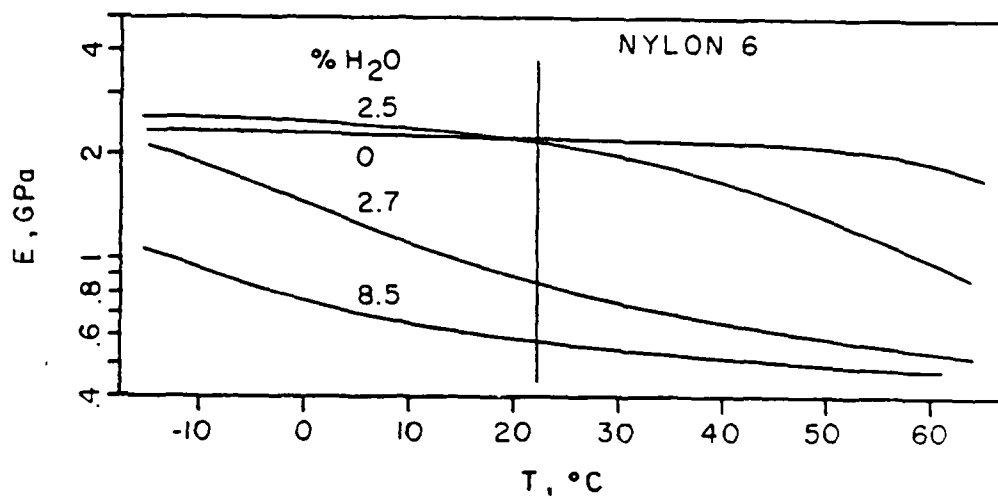


Figure 8 - Modulus as a function of temperature for various moisture levels in N6.

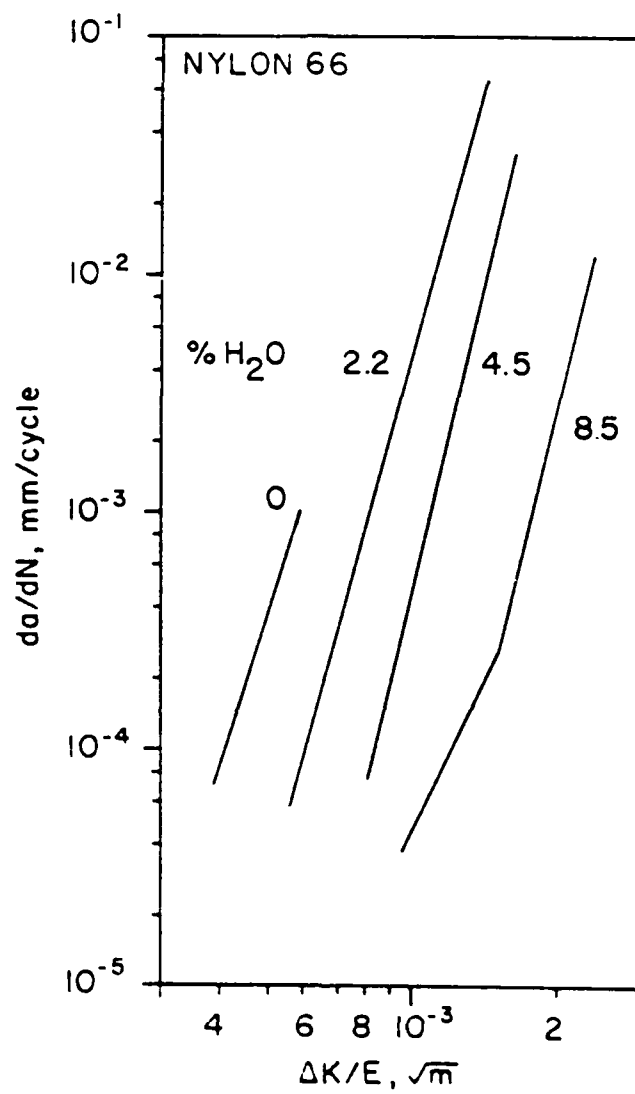


Figure 9 - Fatigue crack growth data for N66 normalized with respect to modulus. ($M_n = 17,000$). (Data from ref. 5)

crack tip blunting and the deleterious effect of modulus degradation. This competition is illustrated schematically in Figure 10. It is seen that, while the blunting mechanism dominates the fatigue response at low moisture levels, the decrease in modulus overshadows crack blunting at higher water contents.

The lack of a crack growth rate minimum in N612 (Figure 6) suggests that a competition between blunting and modulus decrement effects did not exist in this material. In fact, since water saturation in N612 occurs at only 3.2 wt%, as opposed to 8.5% in N66 and N6, the greatest amount of water that N612 imbibed was only slightly greater than the moisture level corresponding to the growth rate minimum in the other nylons. Second, dynamic mechanical data for N612 (Figure 11) show that, even at saturation, the room temperature modulus of N612 decreased by only 30%, in contrast to the 70% decrease in the modulus of N66 (Figure 7a).

The important influence of modulus on FCP behavior can be illustrated in another manner. Referring to Figure 7a, it can be seen that a temperature increase from 22°C to 52°C causes a 40% decrease in the modulus of N66 containing 2.2% water but only a 12% drop in the modulus of dry nylon. Therefore, the expected worsening of FCP response at 52°C should be greater in the moisture-bearing polymer than in dry N66. Indeed, Figure 12 shows that, by raising the test temperature from 22°C to 52°C, the growth rates for an N66 specimen containing 2.6% water increased four-fold, while growth rates in the dry nylon samples increased by only a factor of two. These results confirm the important role that specimen modulus plays in the determination of FCP behavior.

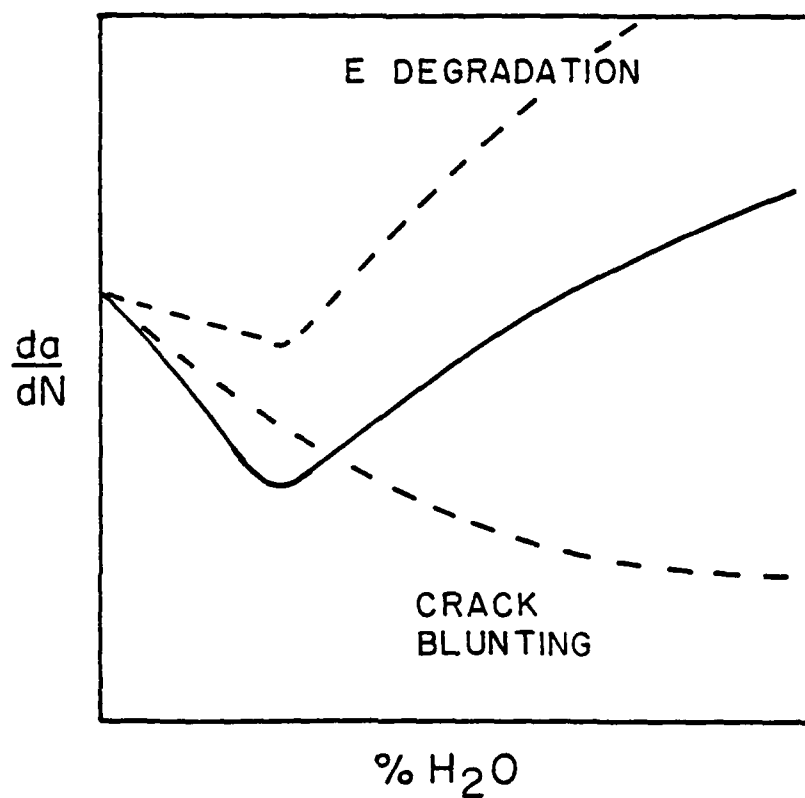


Figure 10 - Schematic diagram of the effect of crack blunting and modulus degradation on crack growth rates in nylon as a function of moisture content.

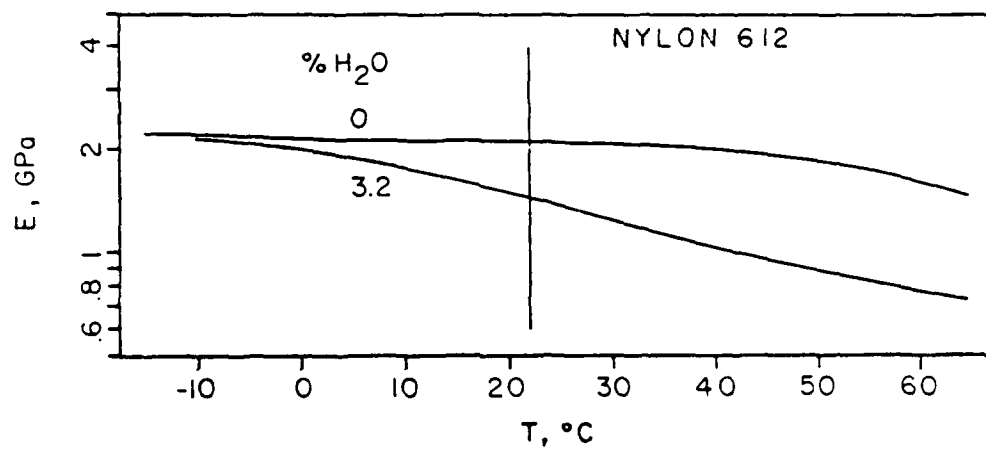


Figure 11 - Modulus as a function of temperature for various moisture levels in N612.

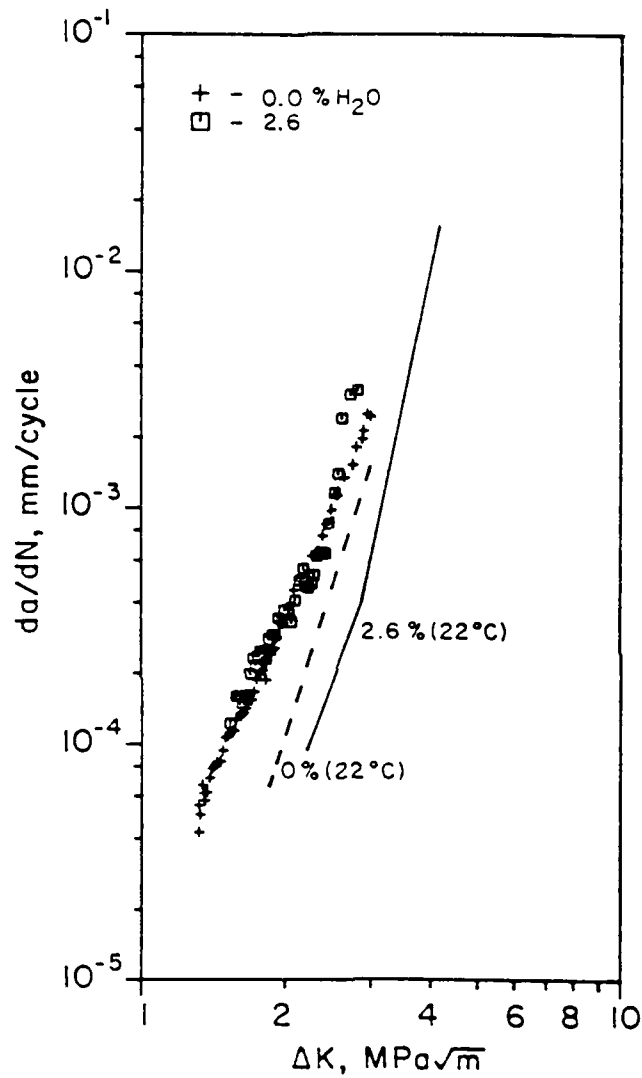


Figure 12 - Crack growth rates in N66 tested at 52°C. Lines represent FCP behavior at 22°C. Note greater shift in the 2.6% H_2O material as compared to dry N66.

Since many of the moisture levels examined in the present research were attained by equilibration in various boiling salt baths (see Tables 1-3), one must examine the possibility that the presence of the salts themselves influenced FCP behavior to some degree. While this cannot be ascertained directly, the following points are relevant. Recently, Burford and Williams [17,18] demonstrated that N66 and N6 were susceptible to stress cracking in the presence of certain inorganic salts. It should be noted that these experiments were performed in the presence of solutions of the inorganic salts, while the presence of any salts during the FCP tests reported here was limited to the amount of salt absorbed during the equilibration procedure. In fact, the amount of salt actually absorbed during equilibration of the fatigue samples was very small. An EDS examination of a fracture surface from a specimen of N66 boiled for 100 hr. in $KC_2H_3O_2$ showed a uniform but barely perceptible amount of potassium across the fracture surface, certainly much less than the fracture surface concentrations found by Burford and Williams [18]. Finally, no evidence of the type of environmental stress cracking described by these authors was found on any of the fatigue fracture surfaces. Therefore, it is concluded that the use of various salts to equilibrate the nylon specimens did not affect the observed FCP behaviors.

Another question to be addressed is the possibility that the boiling procedures used to accelerate equilibration of the nylon specimens caused a reduction in MW by hydrolysis. Viscometric determination of MW for N6 showed that boiling the polymer in water for 190 hr. caused no reduction in M_n from the measured value of 16,000 before the treatment. For N66, the boiling procedure resulted in a 20% drop in M_n from 17,800, the MW of the dry, as-molded polymer. Such a reduction would not be expected to increase the absolute values of FCP rate by an amount greater than the maximum experimental error (a factor of 2), since a 50% reduction in MW from 34,000 to 17,000 previously was found to increase crack growth rates by a factor of only 4 [13]. Furthermore, this 20% reduction in MW should not affect the general shape of the curve of FCP behavior vs. water content.

At the present time, we can only speculate about the reason for the lack of a FCP minimum in N6 as a function of moisture content at ΔK levels greater than 3 MPa/m. It is possible that cyclic-stress-induced hysteretic heating, which would increase with increasing ΔK level, could raise the temperature of the test specimen by a greater amount when the sample contains absorbed water [13]. In turn, this would lead to a relative change in elastic modulus and result in worsened FCP performance.

Conclusions

1. The absorption of small amounts (≤ 2.5 wt%) of water in N66 and N6 decreased crack growth rates, thereby reflecting the ability of tightly bound water to enhance local chain mobility. This increased mobility allows for crack tip blunting as a result of the combined effects of enhanced plastic deformation and localized crack tip heating. However, at higher moisture levels degradation of the room temperature modulus overshadows crack tip blunting and contributes to a general worsening of FCP behavior.
2. Incorporation of water in N612 results in a modest monotonic decrease in crack growth rates, so that saturated N612 is superior to specimens of lower moisture levels. Since the saturation level in N612 (3.2%) is lower than that of N66 or N6 (both 8.5%) and the room temperature modulus at saturation in N612 is much greater than at saturation in the other nylons, FCP behavior of N612 is believed to be dominated by the crack blunting mechanism.

Acknowledgements

The authors wish to thank the Office of Naval Research for partial support of this work and Mr. E. Flexman, DuPont Company for providing plaques of the nylon polymers. The assistance of Ms. S. Webler and Mr. A. Ramirez in characterizing the dynamic spectra, molecular weight and crystallinity of the nylon specimens is greatly appreciated.

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